INVESTIGATION OF THE COMMERCIAL FEASIBILITY OF SEPARATION OF AZEOTROPIC MIXTURES OF N-BUTYL ALCOHOL AND WATER BY GASEOUS DIFFUSION

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SUMMARY

A theoretical investigation of the application of the gaseous diffusion method to the separation of the azeotrope of n-butanol and water into its components has been made. An evaluation of this type of process from a commercial standpoint is presented, and it is concluded that it is not a practicable method for the azeotrope considered.

It is concluded however, that the method may find useful application for separations where it is employed as a last resort.

Calculations have shown that the number of theoretical stages for a cascade to produce a 99.5 weight per cent butanol product from the azeotrope with a cascade waste of 0.5 weight per cent is approximately 10. This assumes an ideal barrier.

Further study of the basic theory is recommended with the aim of developing this method for the separation of other mixtures.

CHAPTER I

INTRODUCTION

Generally speaking, there are three methods for the separating of the constituents of gaseous mixtures which have been developed to wide usefulness in chemical technology. They are (1) separations which are accomplished predominantly by chemical means, (2) processes involving the liquifaction of one or more constituents followed by fractional distillation, and (3) the preferential adsorption and desorption of vapors and gases upon the activated surfaces of solids. Each of these has acquired a more or less special field of usefulness based upon the specific characteristics of the gases to be treated, and each involves recognized disadvantages.

In recent years another method has been developed which under a few special circumstances may be advantageous in preference to the more or less conventional processes already mentioned. It employs the principle of gaseous diffusion, and was developed in connection with the separation of uranium isotopes by the Manhattan District. The method takes advantage of the fact that the average velocities of the molecules of two gases are inversely proportional to the square root of their molecular weights. Accordingly, if a mixture of two gases is confined in a vessel the molecules of each specie in their random motion will collide with the walls at rates inversely proportional to the square roots of the masses. Therefore, if the walls of the container were porous and the pores were just large enough to allow the gases to flow through molecule by molecule an

enrichment in the lighter mass occurs, provided the diffusate is removed as soon as it flows through.

The potentialities and limitations of processes of the diffusional type are brought out by the observation that the physical laws which govern such a process impose an upper limit for its efficiency. Nevertheless, the diffusion process may have application to the separation of mixtures when the separation factor[a] is favorable relative to other methods.

The separation of the constituents of an azeotropic mixture by any of the conventional processes discussed is an especially inefficient and difficult one. It is the purpose of this study to evaluate the gaseous diffusion process for possible use as a commercial method of separation for azeotropic mixtures. The azeotrope of n-butanol and water was chosen for this work because the large molecular weight ratio between the components makes the enrichment by diffusion through a porous wall or "barrier" very large as compared to uranium isotope enrichment by the same process, and consequently fewer stages would be required.

An evaluation is made of the commercial feasibility of such a diffusional process as applied to the n-butanol azeotrope and the fundamental design of a reflux diffusion cascade to produce a 99.5 weight per cent butanol product with a 0.5 weight per cent butanol waste is discussed.

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[a]See page 19.

CHAPTER II

REVIEW OF THE LITERATURE

In late 1941, Dunning, Cohen, and Urey at Columbia University completed the study of the application of the gaseous diffusion method to the separation of the isotopes of uranium. The method had been experimentally demonstrated and the theory for single diffusion units and a cascade of units worked out. From this it was possible to estimate that about 5000 stages would be necessary for one type of diffusion system and that many acres of diffusion barrier would be required to separate a kilogram of U-235 each day.[1] The resulting large scale, spectacular application by the Manhattan District was the climax to the development of the method of separating gases by means of diffusion through porous barriers.

As long ago as 1867 James Clerk Maxwell[2] had shown from considerations of pure probabilities that such a process was possible. He showed that the relative frequency with which molecules of the components of a gas mixture enter a small hole is proportional to their molecular velocities, which are proportional to the square roots of the molecular masses. Even earlier, Graham[3] had discovered the relationship empirically in his studies of the diffusion of gases through porous "plates"

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[1] H. D. Smyth, Atomic Energy for Military Purposes, Princeton University Press, 1945, Princeton, 308 pp.

[2] J. C. Maxwell, "On the Dynamical Theory of Gases," Trans. Roy. Soc., vol. 157, 1867, pp. 49-88.

[3] T. Graham, "On the Motion of Gases," Phil. Trans., vol. 136, 1846, pp. 573-631.

of unglazed porcelain. This relationship has since been known as Graham's law.

This means, if the mol ratio of the light to heavy component of a mixture is R_1 at the upstream end of a hole, the mol ratio of the light to heavy component at the downstream end, R_2, is given by

$$R_2 = R_1 \sqrt{\frac{M_S}{M_L}}$$

where M_S and M_L are the molecular masses of the heavy and light components respectively. There is a limitation placed on this statement, however. This relationship was shown by Knudsen to be true only for the conditions prevailing when the mean free path of the molecules at the upstream end is much larger than the hole diameter and the length of the hole.[4] The "length of the hole," of course, when applied to a diffusion barrier is synonymous to the thickness.

Sullivan and Hertel[5] have shown that for a practical diffusion barrier, the flow is in essential respects similar to flow through a long capillary tube, and quite unlike that of flow through orifices of a thin perforated membrane.

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[4] M. Knudsen, "Die Gesetze der Molekularstromung und der inneren Reibungsstromung der Gase durch Rohren," Annalen der Physik., Ser. 4, vol. 28, 1909, pp. 75-130.

[5] E. O. Kramer, Editor, Advances in Colloid Science, vol. I, Interscience Publishers, Inc., 1942, New York, 434 pp.

MOLECULAR FLOW IN CAPILLARIES

Barrer[6] states that investigations in the field of flow through capillaries have demonstrated that the following phenomena are found in the appropriate region of pressure difference, absolute pressure, and pore size: (1) molecular effusion; (2) molecular streaming or Knudsen flow; (3) Poiseuille or streamline flow; (4) turbulent flow; and (5) orifice flow.

Molecular Effusion

Consider the case of a thin wall in a plane containing a small orifice. The number of molecules N that effuse up to an orifice whose diameter is small compared with the mean free path of the molecules, is given by the following kinetic theory equation:

$$N = \frac{A N_A p}{\sqrt{2\pi M R T}} = \frac{1}{4} A N_A C \left(2\sqrt{\frac{2 k T}{\pi m}} \right) \qquad (1)$$

where A is the area of orifice, C the concentration, k the Boltzmann constant, M the gram molecular weight, m the mass of a single molecule, N_A is Avagadro's number, p the pressure, R the gas constant, and T is the absolute temperature. The parenthetical term represents the mean square velocity.

This equation states that the number of molecules of a gas specie that arrive at the mouth of an orifice is proportional to the area of the orifice and the pressure of the gas, and inversely proportional to

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[6] R. M. Barrer, Diffusion in and Through Solids, The Macmillan Co., 1941, Cambridge, 464 pp.

the square root of the molecular weight. This last relation is identical to Graham's law. It can be seen from this that Graham's law, which was discovered experimentally, can be derived from the kinetic theory of gases.

Molecular Streaming or Knudsen Flow

If a smooth capillary is considered where the molecular collisions with the wall are elastic the flow through the capillary will be made up of all the gas molecules entering it since no molecules are turned back. Therefore, the number of molecules passing through the capillary will be the same as the number diffusing up to the mouth or orifice of the capillary and the flow is the same as that of equation (1) above.

But, the actual behavior in a capillary results in the reflection of some of the molecules from the wall and returned in the direction from which they came. If it is assumed that of each N molecules striking the wall a fraction f are emitted with random velocity distribution, and a fraction $(1 - f)$ are specularly reflected, the following equation can be derived that given the net rate of flow in mols per second through a capillary:

$$\frac{dn}{dt} = \frac{1}{2} \cdot \frac{B}{L} \frac{1}{\sqrt{2\pi M R}} \left[\frac{p_1}{\sqrt{T_1}} - \frac{p_2}{\sqrt{T_2}} \right] \left(\frac{2 - f}{f} \right) \qquad (2)$$

where L is the length of the capillary, f the fraction of molecules emitted with random velocity distribution, M the gram molecular weight, n is mols per second, p_1 and p_2 are the pressures on the high and low pressure sides, respectively, T_1 and T_2 are the high and low pressure side temperatures, and B is the tube shape constant, $\frac{16}{3}\pi r^3$ for circular

tubes where r is the radius.

Poiseuille or Streamline Flow

The following equation gives the rate of flow of a gas through a capillary, when Poiseuille's law is applied (for the case of a compressible fluid obeying the gas law), assuming constant temperature and viscosity and that the capillary is cylindrical:

$$\frac{dn}{dt} = \frac{D^4 \pi}{128 L \mu} \cdot \frac{1}{RT} \cdot \frac{p_1^2 - p_2^2}{2} \qquad (3)$$

where D is the pore diameter, p_1 and p_2 are the pressures on the high and low pressure sides, respectively, μ is viscosity of the fluid, L is length of the capillary, R the gas constant, and T is the absolute temperature. When a correction is made for specular reflection of molecules from the walls the equation becomes:

$$\frac{dn}{dt} = \frac{1}{L} \cdot \frac{3\pi^2 D^3}{32} \cdot \frac{1}{\sqrt{2\pi M R T}} \left[p_1 - p_2\right] \left(\frac{2 - f}{f}\right) \qquad (4)$$

This equation is similar to that of equation (2) above for Knudsen flow. The two equations differ only in the numerical constants. This means that flow by Knudsen's molecular streaming and that of streamline flow bear a ratio to each other of 1.134:1 for cylindrical capillaries. It can be seen therefore, for a constant pressure difference and temperature there is a greater flow of gas by molecular diffusion through a small capillary of given size than by streamline flow through a capillary of even larger size.[7]

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[7] B. S. Gesmer, "An Experimental Study of Promising Diffusion Barriers," Bachelor of Science Thesis in Chemical Engineering, Massachusetts Institute of Technology, 1948.

Turbulent Flow

Turbulent flow is present in a capillary when the mass velocity exceeds a certain limit determined by the Reynold's number. In turbulent flow systems, there is a swirling center mass of fluid which moves along under no direct influence of the walls of the capillary. This center "core" is separated from the frictional drag of the tube surface by a laminar layer of fluid which extends for a short distance from the wall. The translational velocity of the molecules increases from zero (at the wall) to the velocity of the turbulent core. When there is a turbulent core of mass this means the velocity is high or the diameter of the capillary is large. Adequate diffusion barriers will possess a minimum number of areas where there will be turbulent flow. The Reynold's number is directly proportional to the diameter so when there are small pores the flow will be either Poiseuille flow or molecular diffusion.

Orifice Flow

The low pressure end of a capillary can be considered an orifice through which the streaming gas molecules expand adiabatically into a partial vacuum. However, the pressure drop at the orifice is too small to influence the molecular diffusion through the barrier to any extent, as the capillary diameter must be about 0.2 the mean free path of the molecules at the high pressure end. It appears that the phenomenon of orifice flow plays an unimportant part in the overall picture of molecular diffusion through a porous barrier.[8]

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[8]B. S. Gesmer, loc. cit.

Generally, it can be said that at low pressure differentials Knudsen flow (molecular streaming) is present in extremely fine capillaries. The relationship begins to break down when the pore diameter increases above 0.2 to 0.1 of the mean free path in the gas at the maximum total pressure in the pore.[9] The failure is apparently not serious, however, until the pore diameter is about equal to the mean free path. If the pores are larger the phenomena passes into that given by the Poiseuille formula and the separation of constituents by flow becomes negligible.[10] Therefore, to secure high efficiency in the separation of mixtures, all mass or streamline flow must evidently be avoided by the proper choice of menbrane pore size.

Another point of significance is that the flow of molecules decreases with an increase in L, the length of the capillary, due to the friction factor. Gesmer[11] has shown that f (a function of the Reynold's number) in the Fanning equation when considered in the case of capillary flow approaches unity since the Reynold's number is extremely small. The friction $\frac{dF}{dL}$, will be relatively large, and with decreasing pore size, streamline flow will eventually cease entirely and there will be present only molecular streaming expressed by the corrected Knudsen flow equation (2).

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[9] M. Knudsen, loc. cit.

[10] R. S. Mulliken and W. D. Harkins, "The Separation of Isotopes. Theory of Resolution of Isotopic Mixtures by Diffusion and Similar Processes. Experimental Separation of Mercury by Evaporation in a Vacuum," J. Am. Chem. Soc., vol. 44, 1922, pp. 37-65.

[11] B. S. Gesmer, loc. cit.

BARRIER MATERIALS

Early studies of the diffusion method of separating mixtures of gases made use of ceramic type barrier materials. Ramsey and Collie[12] investigated some of the non-homogeneous constituents of helium and argon mixtures using ordinary unglazed clay tobacco-pipe stems. Results were not too satisfactory, however, since the experiments were made at pressures of approximately one atmosphere. Conditions were not favorable at this pressure for very high efficiency, when considered from a diffusion point of view, due to the presence of many oversize pores.

In 1913 Aston[13] employed a similar diffusion tube and reported the first conclusive separation of the isotopes of neon by diffusion. However, he too, encountered the difficulty of having to contend with excessive mass flow through the tube pores resulting in low efficiency. Subsequently, Harkins[14] isolated the isotopes of chlorine with a similar apparatus, by conducting his experiments at reduced pressures which produced a marked increase in efficiency.

In 1932, G. Hertz,[15] utilizing reduced pressure operating conditions and essentially the same diffusion septa as his predecessors,

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[12] W. Ramsey and N. J. Collie, "The Homogeneity of Helium and of Argon," Proc. Roy. Soc., vol. A 60, 1896, pp. 206-216.

[13] F. W. Aston, "A New Elementary Constituent of the Atmosphere," Report of Brit. Assoc. Adv. Science, 1913, p. 403.

[14] W. D. Harkins and A. Hayes, "The Separation of the Element Chlorine into Isotopes (Isotopic Elements)," J. Am. Chem. Soc., vol. 43, 1921, pp. 1803-1825.

[15] G. Hertz, "Ein Verfahren zur Trennung von gasformigen Isotopengemischen und seine Anwendung auf die Isotopen des Neons," Z. Physik., vol. 79, 1932, pp. 108-121.

developed the first multiple effect cascade diffusion apparatus. While making no major additions to the field of barrier development his cascade idea was a revolutionary contribution to the field of gaseous diffusion.

The first reported use of a metallic barrier was made by Warrick and Mack[16] who attempted to perfect a "gas molecule sieve" by removing zinc from a brass disc by a high temperature distillation process at reduced pressures. The idea was to remove the appropriate amount of zinc by the distillation process leaving pores in the material of the proper size to allow the smaller molecules to pass through but retain the larger ones. The molecule sieve did not function satisfactorily.

Recent developments have shown that the metallic barrier is generally more satisfactory. Smyth[17] mentions a barrier made by etching a thin sheet of silver-zinc alloy with hydrochloric acid containing pores of a size 0.01 micron and smaller, as an example.

It is obvious that the choice of barrier is an important one, for the extent of the difference of molecular population density that is maintained on opposite sides of a barrier governs its effectiveness. In a practical diffusion barrier, over-size pores are present to some extent, and any separation process employing it has two types of flow occurring simultaneously. On one hand there is diffusional flow and on the other non-separative mass, or hydrodynamic flow. Use of very dense

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[16] D. L. Warrick and Edward Mack, Jr., "A Copper Membrane Gas-Molecule Sieve. Callendar's Theory of Osmosis," J. Am. Chem. Soc., vol. 55, 1933, pp. 1324-1332.

[17] H. D. Smyth, Atomic Energy for Military Purposes, Princeton University Press, 1945, Princeton, 308 pp.

barrier material in order to reduce mass flow results in reduced capacity. Selection of a barrier therefore requires careful study of the militating factors involved.

RELATED CONTRIBUTIONS

As an outgrowth of the work of Ramsey and Collie,[18] Lord Rayleigh[19] made several significant calculations concerning diffusion processes. He showed that in a simple diffusion process (single stage), diffusing a mixture of gases into a vacuum, the diffusate being formed at any time has a molecular mass less than that of the corresponding residue which becomes more dense, as the diffusion proceeds, by a constant amount. The enrichment of the light fraction is a maximum at the beginning, and the molecular mass of the residue increases indefinitely (in the direction of the heavier constituent's mass), however, in proportion as the logarithm of its quantity decreases, while at the same time the molecular mass of the total diffusate approaches that of the original material. This however, specifies that back diffusion is considered absent.

Present day gaseous diffusion processes are often termed Rayleigh processes as a result of this early study.

Gaede[20] studied the flow of gases through capillaries over the

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[18] W. Ramsey and J. N. Collie, loc. cit.

[19] L. Rayleigh, "Theoretical Considerations Respecting the Separation of Gases by Diffusion and Similar Processes," Phil. Mag. Ser. 5, vol. 42, 1896, pp. 493-498.

[20] W. Gaede, "Die aussere Reibung der Gase," Annalen der Physik., Ser. 4, vol. 41, 1913, pp. 289-336.

entire pressure range for mean free paths much greater than the pore radius to mean free paths much less than the pore radius. From his investigations similar conclusions to those of Knudsen[21] were made. Gaede[22] is also known for the application of the principles of gaseous diffusion to pumps capable of producing a high vacuum. The first diffusion pump was perfected in 1915.

However, Gaede's pump was not used to any great extent, for Langmuir[23] soon afterwards showed that the construction of such pumps could be greatly simplified and many variant designs have resulted. Hertz[24] employed diffusion pumps in his multiple effect cascade with which he succeeded in separating spectroscopically pure forms of the neon isotopes.

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[21] M. Knudsen, loc. cit.

[22] W. Gaede, "Die Diffusion der Gase durch Quecksilberdampf bei niederen Drucken und die Diffusionsluftpumpe," Annalen der Physik., Ser. 4, vol. 46, 1915, pp. 357-392.

[23] I. Langmuir, "A High Vacuum Mercury Vapor Pump of Extreme Speed," Phys. Rev., Ser. 2, vol. 8, 1915, pp. 48-51.

[24] G. Hertz, loc. cit.

CHAPTER III

THE THEORY OF GASEOUS DIFFUSION

If a vessel contains two gases whose relative densities vary from point to point, a process called diffusion will occur in a manner as continually to diminish the inequalities of composition. Due to thermal agitation the molecular motions are such that more molecules of a given kind will travel from a region rich in that kind to a region of scarcity, than travel in the opposite direction. Thus, this process tends to smooth out inequalities of distribution. The net flow of each kind of molecule will take place in the direction in which the density decreases most rapidly. Since, the number of molecules is directly proportional to the pressure, the flow is then seen to be a function of the pressure gradient for the particular gas considered. In addition to this, for a given pressure or concentration gradient, the time rate of change of composition during the diffusive process is influenced by the molecular mass of the specie of molecule considered. That is to say, equalization of distribution will take place for one gas at a greater speed than for the other due to differences in the molecular masses. It has been shown by the kinetic theory and by experiment that the average molecular velocities of gases vary as the inverse square root of the molecular masses.

BARRIER DIFFUSION

Suppose the gas mixture in the vessel considered above were divided into two portions by an intervening porous membrane or barrier. It is seen from the above discussion that for any given component to diffuse across the barrier, there must exist a difference in the partial pressure of the component on the two sides of the barrier. If it is desired to partially separate the mixture discussed, it is apparent that such a separation may be effected by causing the two components to diffuse in the same direction across the barrier. This can be achieved by maintaining a partial pressure difference between the two sides of the barrier as a result of the total pressure difference.

Picture the vessel divided into two portions by the barrier and containing the mixture of two components as represented by Fig. 1

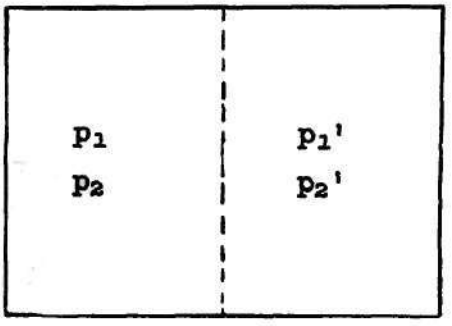

Fig. 1

where p_1 and p_2 are the partial pressures of components 1 and 2 on the left side of the barrier and p_1' and p_2' the corresponding partial pressures on the right side. The rate of diffusion of component 1 through the barrier toward the right is given by

$$k \cdot A \cdot \Delta p_1 \sqrt{\frac{1}{M_1}} \qquad (1)$$

Similarly for component 2, the rate of diffusion is

$$k \cdot A \cdot \Delta p_2 \sqrt{\frac{1}{M_2}} \qquad (2)$$

Δp_1, Δp_2, are the differences in partial pressures across the barrier of components 1 and 2, respectively. A is the area of the membrane and k is a proportionality constant dependent on the characteristics of the membrane and the temperature. A and k are the same for both components 1 and 2. The ratio of 1 to 2 passing the barrier, found by dividing relationship (1) by (2), is

$$\frac{\Delta p_1}{\Delta p_2} \sqrt{\frac{M_2}{M_1}} \qquad (3)$$

This assumes that there is no mass flow through the barrier and that diffusion by the phenomenon of molecular streaming prevails. The square root of the molecular weight ratio can be replaced by μ, and then the relative diffusion rate of component 1 to that of 2 becomes only a function of the partial pressure differences and μ. It is evident that this means the diffusion rate is a function of the concentration differences and μ. It follows from relationship (3) that the diffusion from left to right may be made a basis of a partial separation of the mixture. The limiting case for this diffusion is that when p_1' and p_2' are zero which means that the right side is maintained at zero total pressure. For this limiting case a mixture will yield a product of maximum possible enrichment in the lighter component. The extent of this enrichment will be dependent on μ and the relative concentrations of the two components

in the original mixture. For partial pressures on the right side greater than zero, it is clearly seen that an enrichment is also possible, but to a lesser extent. When the concentration gradient across the diffusion barrier becomes zero, diffusion ceases, and hence it would be impossible to withdraw from the right side of the vessel, a gas enriched by passage through the barrier. Under these circumstances the enriched gas would diffuse backward through the porous membrane more rapidly than in the desired direction.

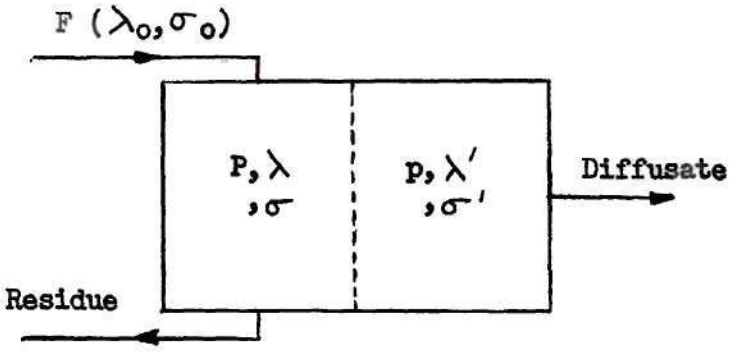

Fig. 2

The device described above would be unsuitable for the separation of gases, as such, due to the fact that, after a time the right section would contain an equal number of molecules of each specie as are present on the left side. Only the first few molecules of gas diffusing through would be enriched for as the concentration of the lighter constituent relative to that of the heavier constituent in the left side decreases, proportionately more and more of the heavier constituent diffuses through. Imagine, however, a system in which the depleted gas in the vessel is constantly being replenished by fresh gas of the original composition, thus maintaining an equimolal concentration within the

container, and only a minute fraction of the gas is allowed to diffuse. This setup can be schematically represented as in Fig. 2. Hence P and p refer to total pressure in the respective chambers of the unit, P being larger than p. It is assumed that the gas flowing into the right chamber is removed as soon as it enters, so that a steady state is reached in which the composition of the gas entering the right chamber is the same as that already there. Thus, by a mechanism of this type a partial separation is made continuously.

The separation effected by a barrier unit of this sort is expressed by a ratio called the separation factor

$$q' = \frac{\lambda'/\sigma'}{\lambda_o/\sigma_o} \quad . \tag{4}$$

Generally, the maximum value q' can have is that of $\sqrt{\frac{M_s}{M_L}}$ or μ when an extended diffusion barrier is not employed. For the case of an extended barrier the undiffused gas can be progressively enriched as it passes along the barrier in much the same way as the plate efficiency in distillation is increased by the progressive flow of the liquid across it. Under these conditions the separation factor is given by Stephens[1] as

$$q' = \frac{1 - (1 - \dot{f})^{\mu}}{\dot{f}(1 - \dot{f})^{\mu - 1}} \tag{5}$$

where $\dot{f}$ is the fraction of the heavy molecular weight molecules that are permitted to pass through the barrier.

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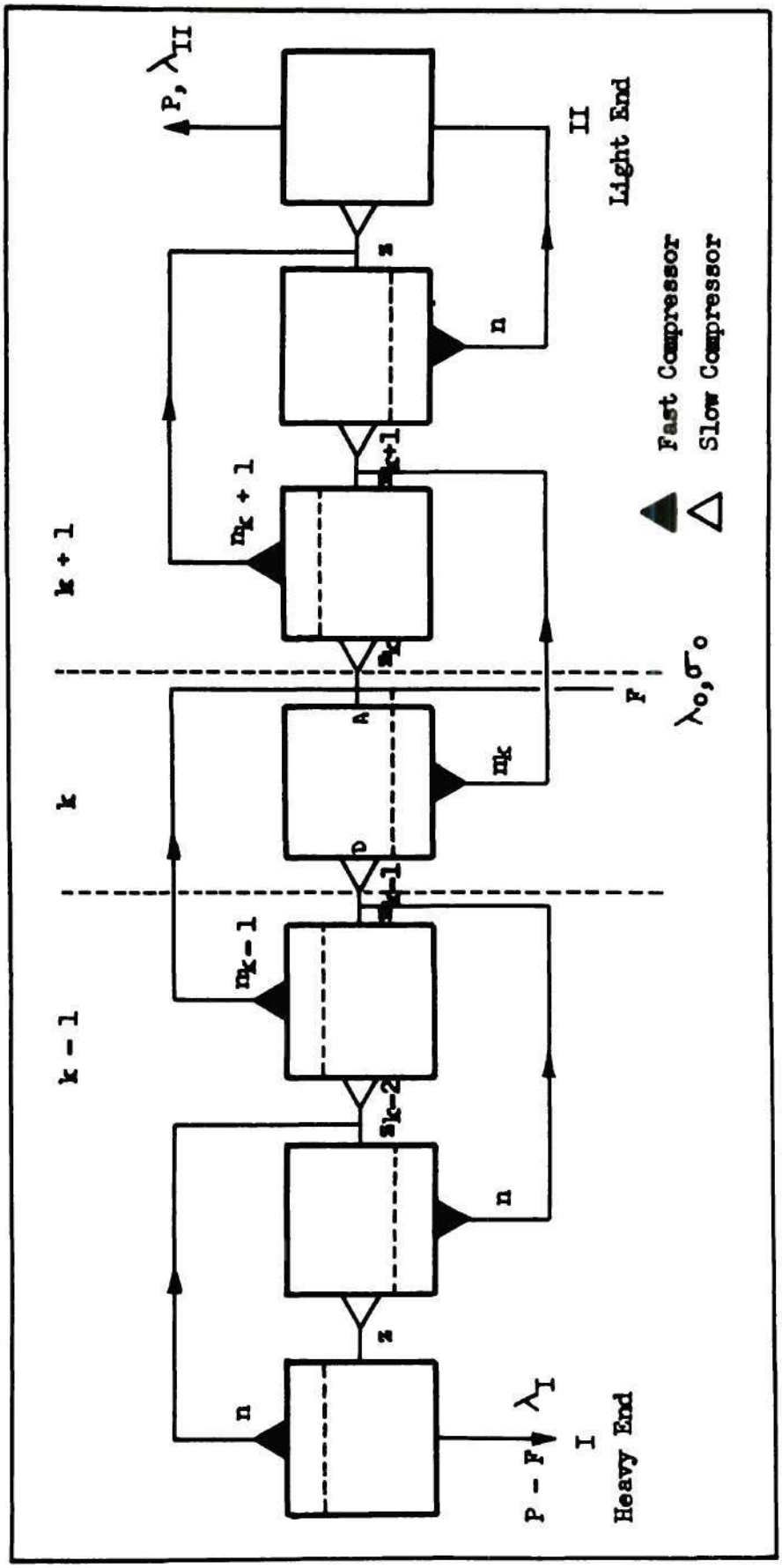
[1] W. E. Stephens, Nuclear Fission and Atomic Energy, The Science Press, 1946, Lancaster, 294 pp.



SCHEMATIC DIAGRAM OF A REFLUX CASCADE

Fig. 3

THE CASCADE[2]

It is readily seen that the degree of separation attained by a single barrier places a limit on the purity of product that can be produced. So in order to obtain as pure a product as might be desired it is necessary to repeat the separation process. A convenient method of accomplishing this is shown in Fig. 3. In the apparatus shown in Fig. 3 the feed enters the chamber or stage designated by k. The gas leaving the stage through the membrane is richer than the feed and enters stage k + 1 as the new feed to be in turn enriched further. The gas leaving the top of k is poorer than the feed, and is sent to k - 1. The gas leaving through the membrane of k - 1 is richer than that entering k - 1 while that leaving the bottom of stage k - 1 is still poorer. By continuing this process by means of further steps, the gas leaving the light end of the cascade can be made as high in the lighter constituent (λ) as desired. Similarly, the heavier constituent (σ) can be enriched on the heavy end. Thus by a suitable application of the principle of refluxing the cascade can be made to yield products at both ends of any desired purity.

The separation factor for a cascade for the light component of a binary mixture is expressed by

$$Q' = \frac{\lambda_{II}/\sigma_{II}}{\lambda_{I}/\sigma_{I}} \tag{6}$$

where the numerals II and I designate the light and heavy component ends

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[2] W. E. Stephens, loc. cit.

of the apparatus. This is expressed in terms of the single stage separation factor as

$$Q' = q'^{Z} \tag{7}$$

q' is the single stage separation factor and is given by

$$q' = \frac{\lambda_k + 1/\sigma_k + 1}{\lambda_k/\sigma_k} = \frac{1 - (1 - f)^{\mu}}{f(1 - f)^{\mu - 1}} \cdot \tag{8}$$

Q, the overall separation factor for the heavy constituent is given by

$$Q = \frac{\sigma_{II}/\lambda_{II}}{\sigma_I/\lambda_I} \cdot \tag{9}$$

The number of mols of the heavy constituent leaving a stage in unit time (at point D) is given by

$$\sigma_{D,k}\, N_{D,k} = \sigma_k (N)_k \exp\left\{ -\frac{\sqrt{2\pi}}{3} \cdot \frac{1}{\sqrt{M_s RT}} \cdot \frac{r}{L} \cdot P_k \cdot \frac{A_k}{(N)_k} \right\} \tag{10}$$

and similarly for the light constituent. Here, $(N)_k$ is the number of mols entering the stage (at point A in Fig. 3) and $(N)_{D,k}$ is the number of mols undiffused gas leaving the same stage. r, is the barrier pore radius, L, the pore length, M is the molecular weight of the component considered, A_k is the barrier area, and P_k is the pressure of the gas entering the stage. In general, P_k is put at 1 atmosphere. The expression employed for the exponent is seen to be that of the Knudsen flow formula for molecular streaming flow through capillaries.[a]

It is evident from equations (5) and (8) that the enrichment of

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[a]See page 7.

the light constituent, or in another manner of expression, the impoverishment of the heavy constituent, is of a logarithmic character. Theoretically, it should be possible to attain an infinite enrichment for a single stage when a value of 1 for $\dot{f}$ is used. However, this is not possible in practice due to back diffusion through the barrier. Stephens reports that it has been found that most efficient flow occurs when a value for $\dot{f}$ of .5 is employed.

CHAPTER IV

APPLICATION TO SEPARATION OF N-BUTANOL-WATER AZEOTROPE

The high molecular weight ratio of the n-butanol-water azeotrope, through a high value of μ, makes the large separation in any one stage great compared to that of the isotopes of uranium. Thus, a small number of total stages, comparatively speaking, would be required with a low proportional cost. A study of this process indicates that it may prove possible to separate constituents of azeotropic mixtures on a commercial scale with a high degree of purity by this means.

Suppose it is desired to produce one pound mol per hour of 99.5 weight per cent butanol from the azeotrope with a 0.5 weight per cent butanol waste product. Complete calculations are presented for this case, assuming an ideal barrier.

METHODS OF CALCULATION

Consideration of the equation from Chapter III relating the single stage enrichment to the overall enrichment of a cascade for the case of the azeotrope n-butanol and water

$$Q' = q'^{Z}$$

can be written as

$$\frac{\lambda_{II}}{\sigma_{II}} \Big/ \frac{\lambda_o}{\sigma_o} = 3.082^{(Z+1)} \qquad (1)$$

for the stages above the feed stage, where λ_{II} is the mol fraction of

the lighter constituent in the top (waste) product P and λ_o is the mol fraction of the lighter constituent in the feed F.

Accordingly, the following relationship can be written for the stages below the feed stage

$$\frac{\lambda_I}{\sigma_I} \Big/ \frac{\lambda_o}{\sigma_o} = \frac{1}{3.082^{Z'}} \tag{2}$$

where λ_I is the mol fraction of the lighter constituent in the product leaving stage No. 1 of the cascade.

These two equations apply to the minimum number of stages to effect a separation by this method and are written with this designation on Z, the number of stages.

For the stages above the feed stage:

$$\frac{\lambda_{II}}{\sigma_{II}} = 3.082^{(Z_{min.} + 1)} \cdot \frac{\lambda_o}{\sigma_o} \tag{3}$$

For the stages below the feed stage:

$$\frac{\lambda_I}{\sigma_I} = \frac{1}{3.082^{Z'_{min.}}} \cdot \frac{\lambda_o}{\sigma_o} \tag{4}$$

Thus, the total number of stages for the cascade is given by

$$Z_{min.} + Z'_{min.} + 1 = \text{Total} .$$

It is necessary to resort to an order of magnitude approximation to determine the yield fraction δ of a process of this type. The yield for the light constituent is roughly expressed by[1]

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[1] W. E. Stephens, loc. cit.

$$\delta \lambda_{II} (N)_{II} \tag{5}$$

where δ is the fraction of the material flowing through the top end of the cascade that is removed as product. λ_{II} designates the mol fraction of the light constituent, and $(N)_{II}$ is the molar flow through the end unit. The numeral II designates the top or light end of the apparatus. A similar expression gives the yield of the heavy constituent at the bottom or heavy end of the apparatus

$$\delta \sigma_{I} (N)_{I} \tag{6}$$

where σ_I designates the mol fraction of the heavy constituent, and $(N)_I$ is the molar flow through the end unit. The numeral I designates the heavy end of the apparatus.

Stephens[2] gives the equation

$$\delta = \theta (q' - 1) \tag{7}$$

for the yield fraction where θ is a production factor calculated from the following relationship for a fractionation process

$$Q'(\theta) = \frac{Q'(0)}{1 + \theta Q'(0)} \cdot \tag{8}$$

$Q'(0)$ is the overall separation factor with no production and $Q'(\theta)$ is the overall separation factor with production. It is seen from this that a production factor must be employed having a negligible effect on the overall separation factor if the given separation is to be achieved.

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[2]W. E. Stephens, loc. cit.

Having determined the fraction δ and knowing the molar yield, calculated for a given feed and specified enrichment, the molar end volumes of the process are simply determined by

$$(N)_{II} = \frac{\text{Yield}_{(\text{Light End})}}{\delta} \tag{9}$$

for the light end yielding the light constituent and

$$(N)_{I} = \frac{\text{Yield}_{(\text{Heavy End})}}{\delta} \tag{9'}$$

for the end yielding the heavy constituent.

The flow through the ends of the process determined, the flow through each stage of the enriching and stripping sections can be calculated by ratio. This can be done since the total number of mols used in the apparatus is constant (excluding the end volumes). The molar flow through the k^{th} stage of the enrichment section is given by

$$(N)_{k} = \frac{\lambda_{II}}{\lambda_{k}} \cdot (N)_{II} \tag{10}$$

where λ_{k} is the mol fraction of the light constituent in the k^{th} stage, and for the stripping section by

$$(N)_{k} = \frac{\sigma_{I}}{\sigma_{k}} \cdot (N)_{I} \tag{11}$$

where σ_{k} is the mol fraction of the heavy constituent in the k^{th} stage.

Having established the molar flow through all stages the following simple material balances permit the calculation of the appropriate values for z and n for the process. Here z and n represent the reflux from the next higher stage and the mols compressed at each stage, respectively.

See Fig. 4 for schematic diagram of the process.

From material balances on the whole cascade the number of mols compressed at the k^{th} stage, n_k, and the total number of mols flowing into the k^{th} stage, $(N)_k$, are given by

$$n_k = z_k + P \tag{12}$$

and

$$(N)_k = n_{(k-1)} + z_k \tag{13}$$

for the stages above the feed stage. Accordingly, for the stages below the feed stage

$$n_k = z_k + P - F \tag{14}$$

and

$$(N)_k = n_{(k-1)} + z_k \tag{15}$$

Equations (12) and (13) and equations (14) and (15) can be combined to give

$$(N)_k = n_{(k-1)} + n_k - P \tag{16}$$

and

$$(N)_k = n_{(k-1)} + n_k - (P - F) \tag{17}$$

for the stages above the feed and below the feed, respectively. These two equations permit the calculation of the mols of gas compressed in the cascade, from which the power consumption required for the process

may be determined.

The area of the barrier for each stage is calculated using the following relation derived from the Knudsen flow formula

$$\ln (1 - \dot{\zeta}) = - \frac{\sqrt{2\pi}}{3} \cdot \frac{1}{\sqrt{M_s RT}} \cdot \frac{r}{L} \cdot (p) \cdot \frac{A_k}{(N)_k} \qquad (18)$$

where $\dot{\zeta}$ is the fraction of heavy molecules diffusing through the barrier, r is the radius of the capillary, L is the length of capillary, (p) is the partial pressure of the heavy constituent (the controlling constituent as far as barrier area is concerned), A_k is the barrier area of the stage under consideration in cm^2, T is the absolute temperature, and M_s is the molecular weight of the heavy constituent.

For purposes of calculation $\dot{\zeta}$ is assumed to be 1/2, L is 10^{-1} cm., r is 10^{-6} cm., p_1 is 1 atmosphere, p_2 is .001 atmosphere for compression calculations, and $\cong 0$ for barrier area calculation. Fixed charges, cost of the azeotrope, and cost of vaporization have been neglected, as have costs of reflux compression. The only costs which are considered are those of pumping from .001 atmosphere to 1.0 atmosphere. The costs which have been neglected seem, in general, to be rather small in comparison with the pumping costs. Isothermal compression has been assumed for simplicity in calculation, though, in actual practice adiabatic compression would be a better approximation, and would, of course, give a proportionately higher cost.

CALCULATION OF NUMBER OF STAGES

Problem: Calculate the number of stages required to separate a 75 mol per cent water - 25 mol per cent n-butanol mixture, producing a fraction from the top of the cascade containing 99.87 mol per cent water (99.5 weight per cent) and a fraction from the bottom of the cascade containing 2.04 mol per cent water (0.5 weight per cent).

From equations (3) and (4)

$$\frac{.9987}{.0013} = 3.082^{(Z_{min.}+1)} \cdot \frac{.75}{.25}$$

$Z_{min.}$ = 3.91 or $\underline{4}$ stages. (Above F)

$$\frac{.0204}{.9796} = \frac{1}{3.082^{(Z'min.)}} \cdot \frac{.75}{.25}$$

$Z'_{min.}$ = 4.41 or $\underline{5}$ stages. (Below F)

Total stages required = 4 + 5 + 1 = $\underline{10}$ stages. Feed enters 6th stage.

DESIGN CALCULATIONS

Problem: Make calculations for the production of 1 pound mol per hour of n-butanol product to determine compression costs.

For the 10 stage cascade as calculated above

$$\lambda_0 = \lambda_8 = 0.75.$$

Then

$$\frac{\lambda_7}{\sigma_7} = 3.082 \times \frac{.75}{.25}$$

$$\lambda_7 = 0.902$$

Or in general,

$$\lambda_k = \frac{1}{\frac{1}{3.082(k-6)} \cdot \frac{.25}{.75} + 1}$$

which gives the following values for λ_k:

λ_1	= 0.01079	σ_1	= 0.98921
λ_2	= 0.032	σ_2	= 0.968
λ_3	= 0.093	σ_3	= 0.907
λ_4	= 0.240	σ_4	= 0.760
λ_5	= 0.493	σ_5	= 0.507
λ_6	= 0.750	σ_6	= 0.250
λ_7	= 0.902	σ_7	= 0.098
λ_8	= 0.966	σ_8	= 0.034
λ_9	= 0.989	σ_9	= 0.011
λ_{10}	= 0.9963	σ_{10}	= 0.0037
$\lambda_{10'}$	= 0.9988	$\sigma_{10'}$	= 0.0012

Feed required

$$.25F = .0012(F - 1.0) + .98921(1.0)$$

$$F = \underline{3.971 \text{ mols/Hour}} \text{ of the azeotrope.}$$

Product at top of cascade

$$.75(3.971) = .01079(3.971 - P) + .9988P$$

$$P = \underline{2.971 \text{ mols/Hour}} \text{ water product.}$$

Product at bottom of cascade

$$P = 1.00 \text{ mol/Hour n-butanol.}$$

For the enrichment section, the overall separation desired is

$$\frac{.9987}{.0013} \quad \frac{.75}{.25} = \underline{256}$$

But have 4 stages instead of 3.91 so actual overall separation factor is

$$\frac{.9988}{.0012} \quad \frac{.75}{.25} = \underline{274}$$

Product may be withdrawn and the separation factor disturbed until it is reduced to 256 and get desired separation in 4 stages. The production factor is determined from equation (8)

$$\underline{256} = \frac{274}{1 + \theta \cdot 274}$$

$$\theta = .0003$$

and

$$\delta = \theta (q' - 1)$$

$$\delta = .00063 \text{ or } \underline{\underline{.001}}.$$

This is fraction of material taken off at top of the cascade. In order to maintain balance it will be necessary to remove a similar fraction from the bottom of the cascade.

The molar flow through the top end of the apparatus is obtained from equation (9)

$(N)_{II}$ = 2975 mols/Hr.

and the flow through stages 6, 7, 8, 9, and 10, is given by equation (10)

$(N)_6$ = 3960

$(N)_7$ = 3295

$(N)_8$ = 3075

$(N)_9$ = 3005

$(N)_{10}$ = 2985

$(N)_{10'}$ = 2975

Similarly, for the bottom end of the apparatus the flow is given by equation (9')

$(N)_I$ = 1000 mols/Hr.

and the flow through stages 1, 2, 3, 4, and 5, is given by equation (11)

$(N)_1$ = 1000

$(N)_2$ = 1022

$(N)_3$ = 1091

$(N)_4$ = 1302

$(N)_5$ = 1951

From equations (13) and (15) the mols compressed in the stages above and below F, respectively are calculated

		Mols Compressed
Stage 6:		
	3960 = 3963 - 3	3963

Stage 7:

3295 = 3298 - 3 -

Stage 8:

3075 = 3078 - 3 3078

Stage 9:

3005 = 3008 - 3 -

Stage 10:

2985 = 2988 - 3 2988

Stage 1:

1000 = 999 + 1 -

Stage 2:

1022 = 1021 + 1 1021

Stage 3:

1091 = 1090 + 1 -

Stage 4:

1302 = 1301 + 1 1301

Stage 5:

1951 = 1950 + 1 -

Total mols compressed: 12351 mols/Hour.

Total work

$$= (12351)\ R\ T\ (2.303)\ \log \frac{1}{.001}$$

or, in KWH

$$= \frac{(12351)(1543)(660)(2.303)(3)(1.356)}{1000 \times 3600} = 32800 \text{ KWH/\#Mol}$$

Cost of power is assumed at $.01/KWH

= $328/Lb. mol n-butanol product.

or

$4.43/Lb. n-butanol product.

The area of the barrier is calculated employing equation (18)

$$\ln (1 - \zeta) = - \frac{\sqrt{2\pi}}{3} \cdot \frac{1}{\sqrt{M_s RT}} \cdot \frac{r}{L} \cdot (p) \cdot \frac{A_k}{(N)_k}$$

From which

$$A_k = \frac{(N)_k \times .301 \times 2.303 \times .10 \times \sqrt{M_s RT} \times 3}{\sqrt{2\pi} \times r \times P_1 (\sigma)}$$

Stage No.	(N)	MF(Heavy Const.)	A (Ft^2)
1	1000	.98921	
2	1022	.968	1.41×10^8
3	1091	.907	1.61×10^8
4	1302	.760	2.28×10^8
5	1951	.507	5.12×10^8
6	3960	.250	2.11×10^9
7	3295	.098	4.46×10^9
8	3075	.034	12.02×10^9
9	3005	.011	36.35×10^9
10	2985	.0037	107.50×10^9

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

From this study the following conclusions can be made:

1. It is definitely possible to separate the components of the azeotrope of n-butanol and water by gaseous diffusion in a limited number of stages.

2. The inherent irreversibility of the gaseous diffusion process makes it unattractive. The thermodynamic efficiency is extremely low.

3. The area of barrier required is exceedingly large although the number of stages is relatively low.

4. Application of the process to the separation of the n-butanol and water azeotrope is not commercially feasible.

It is recommended that:

1. Continued study should be made of the method as to its applicability to the separation of other mixtures for which it might appear to be a last resort expedient.

2. In the event such further study is made and an actual cascade is constructed, that an investigation of the yield fraction versus the overall separation factor be considered.

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